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THE TRANSITION TEMPERATURE OF MANGANOUS CHLORIDE: A NEW FIXED POINT IN THERMOMETRY.

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THE TRANSITION TEMPERATURE OF MANGANOUS CHLORIDE: A NEW FIXED POINT IN THERMOMETRY.

By Theodore W. Richards and Franz Wrede.

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In several previous articles one of us[1] has set forth in detail the advantages of the transition temperatures of crystallized salts as fixed points for thermometry. A number of suitable salts have been suggested, and in particular the sulphate and bromide of sodium have been carefully investigated. For these salts the transition temperatures, referred to the international hydrogen scale, have been found to be, respectively, 32.383° C. and 50.674° C.; and both of these salts have been shown to give points constant and definite enough for convenient use for the above-mentioned purpose.

Among the salts studied by Richards and Churchill in an approximate fashion was manganous chloride ($MnCl_2 \cdot 4H_2O$). This salt has also been investigated roughly by Kuznetzoff, and by Dawson and Williams.[2] All of these investigations were merely approximate; no attempt was made to correct the thermometer for the errors of ordinary thermometry. Therefore they were none of them suitable for defining the point with sufficient exactness for the present purpose. On the other hand all of the investigators agreed in maintaining that the point was constant and definite. Therefore it promises well; and the pres-

[1] T. W. Richards, Am. J. Sci. [4], **6**, 201 (1898); Richards and Churchill, These Proceedings, **34**, 10 (1899); Richards and Wells, These Proceedings, **38**, 431 (1902), **41**, 435 (1906). These four papers are all to be found in full in the Zeitschr. für phys. Chem., the references being respectively **26**, 690 (1898); **28**, 313 (1899); **43**, 465 (1903); **56**, 348 (1906). The present paper also will appear in German in that periodical.

[2] Kuznetzoff, Chem. Centralblatt, 1899, I, 246; Dawson and Williams, Zeit. für phys. Chem., **31**, 59, 1899.

ent paper recites briefly a series of experiments giving much greater definiteness to the point in question and making it available for the verification of thermometers.

Preparation of the Manganous Chloride.

As material for preparation the purest manganous chloride and nitrate of commerce were used. Several preparations made in different ways assured certainty in the product.

The manganous chloride was purified in the first place by crystallization and centrifugal treatment. Through these processes it was passed four times, after solution in ordinary distilled water, and twice after solution in the purest water. Porcelain and platinum dishes were used. This preparation was called I*a*. Two more crystallizations gave I*b*, which was found to have essentially the same transition point. Sample I*c* was made from the two last mother liquors by further recrystallization. This also gave the same point. During these crystallizations traces of iron were found to exist in the otherwise very pure initial salt; these traces disappeared in the very early stages of the crystallization. This was proved by qualitative tests, which were carefully verified by suitable blank determinations.

The purity of the salt, as indicated by the transition temperature, is shown by the following table. Obviously the transition temperature may be used as a guide concerning the freedom of the salt from everything except isomorphous substances, especially for the present purpose. The crude original substance had a transition temperature of 57.91°: the first fraction, 58.03°; the second, 58.05°; the fourth, 58.072°; the sixth, 58.089°; the eighth, 58.090°; and the ninth, 58.089°.

For the preparation of the chloride from the nitrate of manganese, this nitrate was recrystallized until wholly free from iron. It was precipitated as carbonate by means of redistilled ammonium carbonate. This substance was prepared by distillation with water in a platinum condenser and collected in a platinum dish in which the manganous carbonate was precipitated. The precipitate was boiled with many portions of pure water until no more trace of nitric acid was found in the wash water. It was then dissolved in concentrated pure hydrochloric acid and the chloride was three times recrystallized to eliminate the traces of chlorine due to the excess of nitric acid, and also the traces of hydrochloric acid. The salt gave the same transition temperature as the previous sample, although it had been passed through such different treatment. Therefore it seems reasonable to infer that both samples were pure.

It is perhaps worthy of note that manganous chloride has been found by Kahlenberg, Davis, and Fowler[3] to be only very slightly hydrolyzed at 56°, a temperature very near the transition temperature, 58°. The hydrolysis at this temperature is not enough to cause, during the time of the transition experiment, any considerable chance for the formation of the higher oxides of manganese by action of the air on the slightly hydrolyzed solution. This is of course particularly true of the highly concentrated saturated solution at 58°.

Determination of Transition Temperature.

Great care was taken in this work. Besides common thermometers for the determination of the temperature of the thermostat, etc., three instruments of great precision were used.

These were as follows:

1. Normal thermometer (of Jena glass, 59^{III}) about 48 cm. long. The scale of this thermometer extended from 0° to 100° with bulbs between 5° and 18°, and between 65° and 95°. This instrument was made by Richter of Berlin especially for this determination, and was used in the preliminary experiments which were made to show the constancy point of the purest salt. The results are given in the sixth column of Table I. An accident to the thermometer prevented its exact calibration, but its results are exact relatively to one another, and in this respect are just as good as if this calibration had been carried out.

2. A Beckmann thermometer, No. 30, Richter (Jena glass, No. 59^{III}). This thermometer was somewhat larger than usual and made with great care. Its column showed an unusually slight tendency to adhere to the glass, and gave, as will be seen, extraordinarily constant readings. The scale was divided into one-hundredths. All determinations made with the other thermometers were also made with this instrument, which thus served as a means of comparing and controlling them. The results are given in the Tables. The particular point in question, 0.508° on this scale, was standardized with great care by the Physikalisch-Technischen Reichsanstalt and found to correspond to the temperature 58.090° on the international standard. After it had been standardized, the same thermometer was used again for determining the transition temperature, and gave the same results, thus showing that the mercury in the bulb had remained constant in amount under the very careful treatment which it had received.

On account of the breaking of thermometer 1, we desired to confirm

[3] Kahlenberg, Davis, and Fowler, J. Am. Chem. Soc., **21**, 1, 1899.

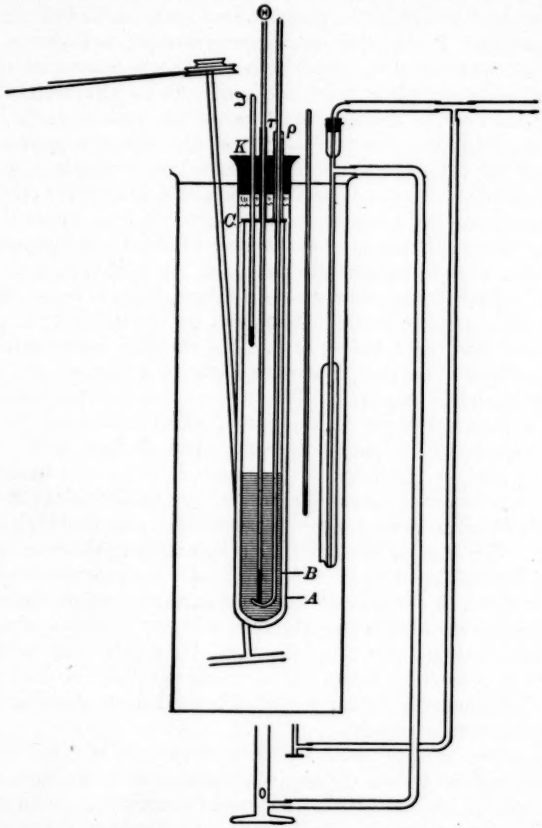
the results of the Beckmann instrument with another carefully standardized normal thermometer which had been directly compared with the standard of the Reichsanstalt. Accordingly another one was procured.

3. Normal thermometer No. 512, Richter (Jena glass, 59^{III}). This thermometer was 65.5 cm. long; the whole scale between 0° and 100° was divided into one-tenth degrees. The scale itself had a length of 57 cm. This instrument was tested with the greatest care in the Reichsanstalt, not only as regards its calibration and behavior under pressure, but also as regards the exact position of particular points, especially the point 59.090°. This was found to read upon this thermometer 58.330°, referred to the hydrogen standard, after correction for the ice point and for external pressure; the error here being +0.240°.

The observed values for the transition point in question, determined with the third thermometer, and also the correction for the temperature of the thread, external pressure, and position of the ice point, are to be found in Table II. Further, in that table are given the exact temperature computed in terms of the hydrogen scale, and also the control determinations made simultaneously with the Beckmann thermometer. The errors of the small extra thermometers for the thermostat, etc., were also carefully determined at this point in their scales.

In order to carry out the determination of the transition temperature with a mercury thermometer, it is necessary to have the stem of the thermometer at the same temperature as the bulb. With high temperature the error, due to neglect of this precaution, may be very great. In determining a transition temperature, it is impracticable to immerse the whole thermometer in the melting mixture; therefore some other device is necessary in order to maintain the thread of the thermometer at the right temperature. In the past we have used two devices for this purpose. In one case the thermometer was surrounded by a glass tube, through which circulated water of the right temperature. This device works very well, except that it is difficult to prevent cooling of the water. The other device consisted in a deep thermostat, above which the thermometer just projected. In the present series of determinations we have altered this latter arrangement by making the thermostat of glass, using a very tall glass beaker 52 centimeters in height and 14 centimeters in diameter, surrounded at the sides with asbestos paper and with long narrow windows in front and behind for observation. A sketch of this apparatus is given in the accompanying diagram. Into the water was immersed, quite to its top, a strong, very large tube (A) closed below, of about 5 centimeters diameter. In this there was contained, isolated by pieces of cork, the slightly smaller

tube (B) designed to contain the substance. This tube, and also the stirrer, were made out of good insoluble glass. Because the mercury-thread, which we needed to consider, was 2 centimeters shorter than



the second tube, it was contained entirely within it when the thermometer was raised about a centimeter above the bottom of the tube. This inner tube was closed by a cork cover (C), which was bound by means of two small glass tubes (τ and ρ) to the cork stopper (K) of the outer tube. The two little tubes binding these two pieces of cork

served to admit the thermometer (Θ) and the stirrer. The temperature in the outer very large tube fluctuated but very slightly, and that in the inner tube containing the substance was almost exactly constant. There was no difficulty in regulating the heat of the water in the thermostat to within less than one tenth of a degree by an ordinary gas regulator. For reading the thermometer (Θ), a telescope with a very exact micrometer was used, by means of which the smallest scale divisions could easily be divided into hundredths. The danger of irregular readings of the thermometer through the various media, which might cause errors due to parallax, was wholly overcome, in that on the one hand all the glass walls were arranged as vertically as possible, and the telescope was made exactly horizontal, and on the other hand every reading of the thermometer was made both from before and from behind. Obviously, the mean of these two readings must represent the true value, even if a slight displacement due to refraction had been present. The thermometer was so arranged that it could easily be turned on a vertical axis, so that there was no difficulty in making these readings. As a matter of fact, the readings before and behind never differed more than four thousandths of a degree, and usually differed much less than that. The true value was always taken as the mean of these readings. In the case of the Beckmann thermometer, the telescope was so placed that the scale division lines appeared perfectly straight through the tube, without a trace of bending.

The concordance of the results furnishes yet another proof that these methods of reading were entirely satisfactory and thoroughly trustworthy. The great advantage of this apparatus is that the temperature of the scale can be kept indefinitely at a temperature as nearly as possible to the true value, and this is no small advantage, because with such a length of thread a single tenth of a degree difference of temperature causes a thread-correction of $\frac{1}{1000}°$. We conclusively proved that it was not possible to attain the necessary constancy if even a millimeter of the mercury thread projected beyond the thermostat into the temperature of the room.

As has been said, in Table I the accurate results with the first thermometer and the Beckmann are given, and also the corrections, in so far as these could be determined. The final determinations with the large new thermometer are given in Table II. On the basis of these results, we think it is safe to say that the transition temperature of manganous chloride for the transition from the crystal form with 4 molecules of water into that with 2 of water, has a value 58.089° (± 0.005) referred to the international hydrogen scale.

In conclusion, it is a great pleasure to express our thanks to the

TABLE I.

Preparation No.	Thermometer I.					Reading of Beckmann Thermometer.	Corrected Press.	Result corrected to H_2 Standard (Reichsanstalt).
	Observed Reading.	Correction ($\frac{1}{1000}$°).			Result not corrected to H_2 Standard.			
		Thread.	Ice.	Press.				
I*a*	58.087	−2	0	−1	58.084	0.5078	−1	58.089°
	58.081	−2	+3	−1	58.081			
	58.077	−2	+5	−1	58.079			
	58.077	−2	+7	−1	58.081			
					58.081			
I*b*	58.084	−1	0	−2	58.081	0.5079	−2	58.088
	58.084	−1	0	−2	58.081			
	58.085	−2	+3	−2	58.084			
					58.082			
I*c*	58.077	−2	+5	−2	58.078	0.5081	−1	58.089
	58.081	−1	+5	−2	58.082	0.5082	−1	58.089
	58.083	−1	+3	−2	58.083			
					58.081			
II	58.089	−5	+3	−2	58.085	0.5075	−1	58.089
	58.089	−4	+3	−2	58.086			

TABLE II.

	New Thermometer.							
I*b*+I*c*	58.334	−2	+3	−2	58.332			
+II	58.330	−0						
	58.334	−6			58.329			
	58.330	−2	+3	−2		0.5072°	−1	58.088
					58.331			
					= 58.091° cor.			
I*b*	58.324	−0	+7	−1	58.330	0.5076°	−1	58.089
					= 58.090° cor.			
Total . . . . . 58.089°								

Director of the laboratory, Professor Emil Fischer, and to the President of the Physikalisch-Technischen Reichsanstalt, Professor Warburg, for their interest in and support of this investigation, and to Dr. Grützmacher of the Reichsanstalt for his prompt and thorough testing of our thermometer.

Summary.

1. For the transition temperature of manganous chloride from the tetrahydrate to the dihydrate the point 58.089° upon the international hydrogen scale has been found. This point is probably not more than 0.005 degree in error.

2. This transition temperature of manganous chloride was found to be suitable for serving as a fixed point in thermometry, on account of the ease of preparation of the salt and the satisfactory definiteness of the transition.

3. In this paper is described a tall transparent thermostat which makes it possible to determine exactly the temperature of the whole length of the thermometer.

First Chemical Institute of the
University of Berlin,
August 1, 1907.